# Mononuclear Schiff Base Complexes Derived from 5-Azophenylsalicylaldehyde with Co(II), Ni(II) Ions: Synthesis, Characterization, Electrochemical Study and Antibacterial Properties

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**ABSTRACT**

**In the present research, 1,2-di[*N*-2-phenylthio-5-azophenylsalicylidene]ethane (H₂L¹), 1,3-di[*N*-2-phenylthio-5-azophenylsalicylidene]propane(H₂L²) and 1,4-di[*N*-2-phenylthio-5-azophenylsalicylidene]butane (H₂L³) were synthesized. ML¹, ML² and ML³ complexes were prepared through the reaction of H₂L¹, H₂L² and H₂L³ with Ni(II) and Co(II) acetate salts. The prepared ligands and their complexes were characterized with FT-IR, ¹H-NMR, elemental analysis, conductivity and magnetic measurements, ESI-mass, UV-Vis spectroscopy and cyclic voltammetry. The complexes had monomeric structure according to the mass spectral data. All of the complexes had a six-coordinated octahedral geometry. The electrochemical behavior of the ligands, Ni(II) and Co(II) complexes was investigated by CV in DMF under argon atmosphere. The results show that the coordination of Ni(II) causes the ligands to be deactivated. The voltammogram of Co(II) complexes shows that the reduction of CoL¹ is harder than CoL³ and CoL² is inactive. Their antibacterial activity was investigated and the complexes exhibited better antibacterial activity than the free ligands against selective bacteria.**

**KEYWORDS**

**Schiff base complexes, 5-azophenylsalicylaldehyde, electrochemical study, antibacterial properties.**

## 1. Introduction

Schiff bases are synthesized through the reaction of primary amines and aldehydes or ketones. Schiff bases are extensively used as ligands in as much as their high stability and appropriate solubility in common solvents. Frequently, a geometrical constriction is imposed by the $\pi$-system in a Schiff base which it affects the electronic structure as well.[1] The characteristics of metal complexes including Schiff base ligands and their wide applications have aroused significant attention. Schiff base complexes is a fast-growing field due to the numerous possible structures for the ligands varying with the aldehyde and amine used.[2] Schiff base complexes have some properties like antibacterial,[3] antifungal,[4] anticancer,[5] antioxidant,[6] anti-inflammatory,[7] antimalarial,[8] antiviral activity,[9] and are used in oxygen storage devices,[10] molecular architectures,[11] lasers,[12] OLED applications,[13] transistors[14] and fluorescent sensors as well.[15]

Interest in the chemistry of nickel compounds have been grown in a great manner due to the finding of sulfur donor ligands to nickel in various metalloenzymes.[16–19] The development of coordination chemistry and bio-mimetic chemistry are somehow dependent on molecules containing O, N, S donor sites. Specially, $N_2O_4$ and $N_2O_2S_2$ binding cores containing non-cyclic hexadentate ligands are greatly suitable for this purpose.[20] The reaction of a Co(II) salt with 1,2-di[*N*-phenyl-thio-5-azophenylsalicylidene]ethane led to the oxidative cleavage of the ligand, instead of forming a simple complex. C–S bond cleavage is common, especially when elements of cobalt group is used in the presence of cyclic thioether ligands and some non-cyclic ones as well. The purpose of the current research is to prepare and investigate the structure of H₂L¹, H₂L² and H₂L³ Schiff base ligands with Co(II) and Ni(II) ions (Scheme 1).

In addition, the electrochemical properties of the prepared ligands and complexes were studied by cyclic voltammetry. Furthermore, the antibacterial effect of prepared ligands and complexes were investigated on some clinically significant bacteria like *Staphylococcus aureus*, *Escherichia coli* and *Bacillus subtilis*.

Our group interest in the synthesis of Schiff base is motivated by the fact that Schiff bases are one of the important classes of organic compounds with a broad range of biological properties. They are often used as chelating ligands in the field of coordination chemistry and when complexed with different metals, they exhibit a broad range of biological activities, including antimalarial, antibacterial, antifungal, etc. Furthermore, bacterium and fungi have developed resistance to the current line of treatment recently, which has to be of concern. Accordingly, novel Schiff bases with new properties and better performance is our main aim.
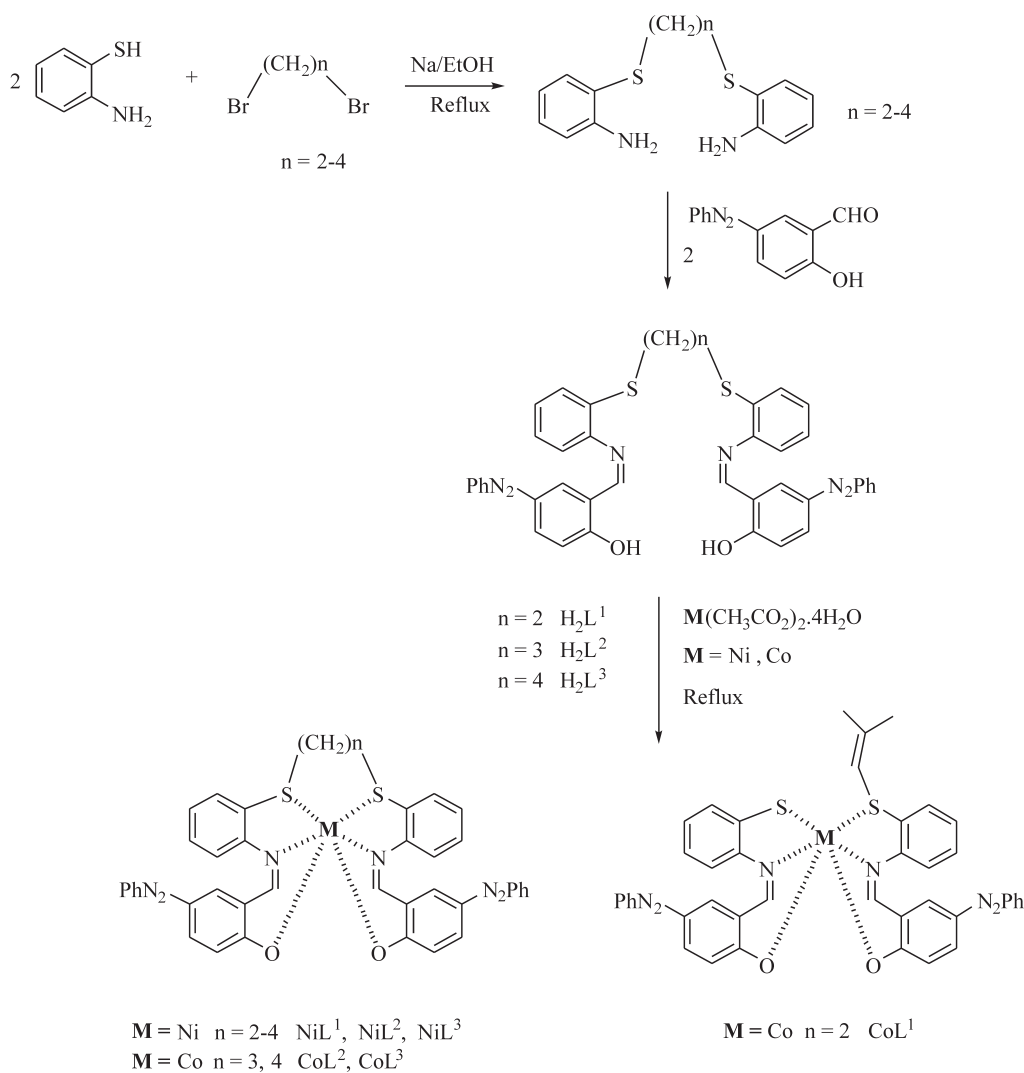
## 2. Experimental

### 2.1. Materials

All reagents were purchased from Merck and were used without further purification. 5-Azophenylsalicylaldehyde (**1**), 1,2-di(*o*-aminophenylthio)ethane (**2**), 1,3-di(*o*-minophenylthio)propane (**3**) and 1,4-di(*o*-aminophenylthio)butane (**4**) were synthesized according to published procedure.[20]

**Scheme 1**
Synthesis route of Schiff base ligands and their complexes.

## 2.2. Physical Measurements

CHNS analyses were conducted through an Elemental Vario EL III elemental analyzer. Electronic spectra were recorded in DMF solvent with a Shimadzu, UV-1650 PC spectrophotometer. FT-IR spectra were obtained by using KBr pellets on a Bruker Tensor instrument. Conductance measurements were conducted in DMF solvent with a Metrohm 712 conductometer. $^1$H-NMR spectrum were obtained with a Bruker Avance, 400 MHz, ultrashield in CDCl$_3$ as a solvent and Me$_4$Si as internal standard. Mass spectra of all compounds were recorded using LCMS-2010A of make Shimadzu. A vibrating sample magnetometer (Model PAR 155) was used to measure the magnetic susceptibility that was done at room temperature. Cyclic voltammetry (CV) measurements were carried out with an Autolab potentiostat PGSTAT 302 Eco Chemie. Melting points of the ligands and complexes were determined by using the finely powdered sample in a fused capillary using Elico melting point apparatus. The antimicrobial studies of the Schiff bases and the complexes were carried out by disc diffusion method.

## 2.3. Synthesis

### 2.3.1. *Ligands Preparation*

10 mmol (2.76 g, 2.90 g and 3.04 g for **2**, **3** and **4,** respectively) of diamine solution in 15 mL of absolute ethanol was added to the solution of compound **1** (20 mmol, 4.52 g) in ethanol/dichloromethane (5:1) (12 mL). In addition, 1 drop of glacial acetic acid was added to the aforementioned solution. The resultant mixture was kept under stirring and reaction under reflux condition for 1 h. The yielded precipitate (orange colour) was filtered out followed by washing using ethanol and ether and recrystallization from CH$_2$Cl$_2$ for H$_2$L$^1$, H$_2$L$^3$ and CH$_2$Cl$_2$/EtOH for H$_2$L$^2$, respectively.

### 2.3.2. *Cobalt(II) Complexes Preparation (CoL$^1$, CoL$^2$, CoL$^3$)*

1 mmol (0.249 g) of Cobalt(II) acetate tetrahydrate was added to 30 mL of ethanol, after which the obtained solution was added to a heated suspension of H$_2$L$^1$, H$_2$L$^2$ or H$_2$L$^3$ (1 mmol) in 10 mL of dichloromethane. Then, the prepared mixture was heated under vigorous stirring to accomplish the reaction for 4 h. In the next step, a rotary evaporator was used to evaporate the solvent in order to reduce its volume to 10 mL. Finally, collecting of the products were carried out by filtration and recrystallization from CH$_3$CN/CH$_2$Cl$_2$ (1:1) for CoL$^1$ and CoL$^3$ and from petroleum ether/CH$_2$Cl$_2$ (1:1) for CoL$^2$.

### 2.3.3. *Nickel(II) Complexes Preparation (NiL$^1$, NiL$^2$, NiL$^3$)*

For this purpose, 1 mmol (0.248 g) of Ni(CH$_3$COO)$_2$.4H$_2$O was added to 30 mL of ethanol, then the solution was added to a hot

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suspension of $H_2L^1$, $H_2L^2$ or $H_2L^3$ (1 mmol) in dichloromethane (10 mL). The obtained mixture was kept under stirring and heating under reflux for about 4 h. The solvent was evaporated using a rotary up to 10 mL. In the end, collection of the products was carried out by filtration and recrystallization $CH_3CN/CH_2Cl_2$ (1:1) for $NiL^1$, $NiL^2$ and $NiL^3$. The physical properties of ligands and complexes are tabulated in Table 1. Nevertheless, suitable crystals could not be prepared for single crystal diffraction studies.

### 2.3.4. *Investigation of Antibacterial Activity by Disc Diffusion Method*

The ligands and synthesized metal complexes were screened for antibacterial activity against pathogenic bacterial species *Escherichia coli*, *Staphylococcus aureus*, *Bacillus subtilis* and comparisons were made. The paper disk diffusion method was adopted for the determination of antibacterial activity.[21] This method is simple and is routinely used in hospital laboratories. The ligand/complex (30 $\mu$g) in DMF (0.01 mL) was placed on a paper disk (Whatman-model), with 5 mm in diameter with the help of a micropipette. The disks were left in an incubator for 48 h at 37 °C and then were applied to the bacteria grown on agar plates. For the preparation of agar plates for bacterial species, Mueller-Hinton agar with 2 % of glucose (50 g), obtained from Merck, was suspended in freshly distilled water (1 L). It was allowed to soak for 20 min and then was boiled in a water bath until the agar was completely dissolved. The mixture was autoclaved for 15 min at 120 °C, poured into sterilized Petri dishes, and then stored at 40 °C for inoculation. Inoculation was performed with a platinum wire loop that was made red hot in a flame, cooled, and then used for the application of bacterial strains. Each paper disk was placed on an already inoculated agar plate which was then incubated at 37 °C for 18 h. Activity was determined by measuring the diameter of zones showing complete inhibition (mm).

## 3. Results and Discussions

### 3.1. FT-IR Spectra of Ligands and Complexes

Although the single X-ray crystallography is a powerful technique, infrared spectra is an alternative as a suitable method to obtain sufficient information for clarifying the nature of bonding. Obtained IR bands are shown in Table 2. In the spectra associated to $H_2L^1$, $H_2L^2$ and $H_2L^3$ strong absorption bands can be seen at 1611–1618 cm$^{-1}$ that could be associated to the C=N bond,[22] confirming the successful synthes of the Schiff base. Moreover, the absence of C=O and N-H peaks, indicates Schiff bases condensation. In addition, a broad band centred at around 3440–3446 cm$^{-1}$ is due to $\nu$(OH) of the phenolic hydroxyl group.[23] The reaction of Ni(II) and Co(II) acetate salts with the Schiff bases ($H_2L^1$, $H_2L^2$, $H_2L^3$) yield $NiL^1$, $NiL^2$, $NiL^3$ and $CoL^1$, $CoL^2$, $CoL^3$ complexes. The C–O stretching vibration appeared as a weak band within the 1279–1286 cm$^{-1}$ for the free ligands and in the 1330–1388 cm$^{-1}$ region for the complexes. In the spectra related to complexes, the C–O peak was shifted to higher frequency that indicates the formation of oxygen bond between phenolic group and the metal ions.[24] Furthermore, $\nu_{C=N}$ peak was shifted to lower frequencies in compare to free Schiff bases, showing a decrease in its bond order. This phenomenon is because of the coordination bond of the metal with the imine nitrogen lone pair.[22] According to the results, it was possible to come to a conclusion that the binding of the OH group was the reason for disappearance of the corresponding $\nu_{O-H}$ vibration existing in the precursor ligands spectra.[25] The $CoL^1$ complex showed a strong $\nu_{C=C}$ vibration related to the –S–HC=CH$_2$ moiety formed as a result of the C–S bond cleavage at 1525 cm$^{-1}$ that was not seen in the other complexes. All of the obtained data suggested that the metals were bonded to the Schiff bases with the phenolic oxygen and the imine nitrogen. At lower frequency the complexes exhibited bands around 359–387 cm$^{-1}$ which are assigned to $\nu_{M-S}$ vibration mode.

**Table 1** Physical and analytical data of the ligands and complexes.

| Molecular formula | Molecular weight /g mol$^{-1}$ | Yield /% | $\Lambda_m$ /W$^{-1}$ cm$^{-1}$ mol$^{-1}$ | M.p. /°C | Elemental analysis found (Calcd.) | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | C /% | H /% | N /% | S /% |
| $C_{40}H_{32}N_6O_2S_2$ ($H_2L^1$) | 692.20 | 56 | – | 224 | 69.25 (69.36) | 4.48 (4.62) | 11.97 (12.13) | 9.16 (9.24) |
| $C_{41}H_{34}N_6O_2S_2$ ($H_2L^2$) | 706.22 | 62 | – | 221 | 69.55 (69.68) | 4.63 (4.81) | 11.60 (11.89) | 8.90 (9.06) |
| $C_{42}H_{36}N_6O_2S_2$ ($H_2L^3$) | 720.23 | 67 | – | 200 | 69.86 (70.00) | 4.94 (5.00) | 11.51 (11.66) | 8.61 (8.88) |
| $C_{40}H_{29}N_6O_2S_2Co$ ($CoL^1$) | 748.11 | 83 | 115 | >270 | 62.31 (62.45) | 3.87 (3.96) | 10.25 (10.40) | 7.79 (7.93) |
| $C_{41}H_{32}N_6O_2S_2Co$ ($CoL^2$) | 763.14 | 77 | 8.994 | 300< | 64.22 (64.48) | 3.99 (4.19) | 10.92 (11.01) | 8.24 (8.38) |
| $C_{42}H_{34}N_6O_2S_2Co$ ($CoL^3$) | 777.15 | 97 | 4.590 | >245 | 64.70 (64.87) | 4.25 (4.37) | 10.69 (10.81) | 8.19 (8.23) |
| $C_{40}H_{30}N_6O_2S_2Ni$ ($NiL^1$) | 748.12 | 69 | 1.778 | >325 | 63.99 (64.11) | 3.90 (4.00) | 11.14 (11.21) | 8.37 (8.54) |
| $C_{41}H_{32}N_6O_2S_2Ni$ ($NiL^2$) | 762.14 | 67 | 3.945 | 255< | 64.38 (64.50) | 4.10 (4.19) | 10.93 (11.01) | 8.13 (8.39) |
| $C_{42}H_{34}N_6O_2S_2Ni$ ($NiL^3$) | 776.15 | 78 | 2.686 | >268 | 64.75 (64.88) | 4.23 (4.37) | 10.68 (10.81) | 8.19 (8.23) |

**Table 2** IR spectral data of Schiff base ligands and their metal(II) complexes.

| Compound | $\nu_{O-H}$ | $\nu_{C-H\ (aromatic)}$ | $\nu_{C-H\ (aliphatic)}$ | $\nu_{C=N}$ | $\nu_{C=C\ (-S-C=CH2)}$ | $\nu_{M-S}$ | $\nu_{C-O\ (phenolic)}$ |
|---|---|---|---|---|---|---|---|
| $H_2L^1$ | 3446 | 3051 | 2922 | 1612 | – | – | 1280 |
| $H_2L^2$ | 3445 | 3047 | 2950 | 1619 | – | – | 1286 |
| $H_2L^3$ | 3441 | 3055 | 2928 | 1613 | – | – | 1283 |
| $CoL^1$ | – | 3057 | 2961 | 1603 | 1525 | 387 | 1331 |
| $CoL^2$ | – | 3057 | 2922 | 1604 | – | 375 | 1333 |
| $CoL^3$ | – | 3057 | 2924 | 1605 | – | 380 | 1333 |
| $NiL^1$ | – | 3064 | 2922 | 1607 | – | 364 | 1348 |
| $NiL^2$ | – | 3055 | 2962 | 1605 | – | 359 | 1384 |
| $NiL^3$ | – | 3060 | 2928 | 1607 | – | 361 | 1388 |

## 3.2. Conductance Measurements

The molar conductance of the complexes was measured for $10^{-3}$ M solutions in DMF at 26 °C. The results indicated that all complexes (except CoL[1] which is an electrolyte) are non-electrolytes in DMF.[26,27] According to the results (Table 1), $H_2L^1$, $H_2L^2$ and $H_2L^3$ Schiff bases were coordinated to the Ni(II) and Co(II) ions as doubly negatively charged anions. Hence, the deprotonation of two phenolic OH has generated oxygen anions that were bonded to the metal ions.

## 3.3. Magnetic Moments

The magnetic moments for the Ni(II) complexes were in the range of 2.83–2.90 B.M which were consistent with the octahedral stereochemistry and the magnetic moments of Co(II) complexes (CoL[2], CoL[3]) were found to be 4.83 and 4.91 B.M, respectively. The values confirmed that the Co(II) complexes had octahedral geometry (Table 3).[28] Magnetic susceptibility measurement exhibited that the CoL[1] is diamagnetic, supporting the +3 oxidation state of the cobalt.

## 3.4. Mass Spectra of the Compounds

The ESI–mass spectra were measured to confirm the composition and the purity of the complexes and ligands under investigation (Table 4). The obtained mass spectra showed molecular ion peaks, which were matching with the expected values.

## 3.5. Electronic Spectra

All spectra were recorded in DMF ($10^{-3}$ M) at room temperature. Obtained results are shown in Table 5. The ultraviolet absorption spectrum of the Schiff base ligands demonstrated two bands positioned at 269–273 and 344–369 nm assigned to $\pi \rightarrow \pi^*$ (phenyl ring) and $n \rightarrow \pi^*$ (-C=N) group.[29] A shift was seen to blue regions in all complexes that confirms the coordination of the ligand to the metal. Moreover, $d \rightarrow d$ transitions led to some new bands for the complexes in the visible region. Co(III) is a $d^6$ system and complexes can be high spin or low spin depending

upon the type of the ligand. For $d^6$ high spin (four unpaired electron) case, the ground state term is $^5D$ which is split into $^5T_{2g}$ and $^5E_g$ states so the transition can be assigned to $^5T_{2g} \rightarrow {}^5E_g$ while for $d^6$ low spin case, the ground state is $^1A_{1g}$ and there are two singlet excited states, $^1T_{1g}$ and $^1T_{2g}$ and the two observed spectral transitions are assigned as $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$. The electronic spectrum for synthesized Co(III) complex (CoL[1]) showed two bands which are assigned to $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ transition with octahedral geometry around central Co(III). The absorption spectrum of Co(II) complexes exhibited two bands at $\lambda_{max} = 405$–416 nm and $\lambda_{max} = 577$–586 nm. These bands correspond to the $^4T_{1g(F)} \rightarrow {}^4T_{1g(P)}$ and $^4T_{1g(F)} \rightarrow {}^4A_{2g(F)}$ transitions, respectively, that confirm the presence of an octahedral structure around Co(II) ion.[30,31] Ni(II) complexes exhibit three bands which are assigned to $^3A_{2g(F)} \rightarrow 3T_{2g(F)}$, $^3A_{2g(F)} \rightarrow {}^3T_{1g(F)}$ and $^3A_{2g(F)} \rightarrow {}^3T_{1g(P)}$ transitions, respectively. Since the transition $^3A_{2g} \rightarrow {}^3T_{1g(P)}$ generally occurs in the region of 330–400 nm in which the bands due to organic fraction of the complexes arise as well, hence this region is not useful from the point of view of drawing any conclusion about the stereochemistry around the Ni(II) centre. However, the first two low-energy bands observed in the region of 400–900 nm in all of the complexes are characteristic of nickel(II) in octahedral environment.

## 3.6. ¹H NMR Spectral Studies

In the all ¹H-NMR studies, chloroform was used to record the spectra. In the obtained spectra of the ligands, the singlet resonances in the $\delta = 13.77$–13.80 ppm and multiplet peaks at $\delta = 7.88$–8.21 ppm regions could be related to the protons of the phenolic OH groups,[20] and aromatic protons[32], respectively. Additionally, azomethine group protons exhibited singlet signals in the range of $\delta = 8.70$–8.73 ppm in all of the spectra of the ligands.[33] Also, aliphatic protons showed some multiple signals in the range of $\delta = 1.25$–3.16 ppm.[23] No signals were observed in the spectrum related to the free amino and aldehyde groups that confirms the formation of the Schiff base ligands. The ¹H-NMR spectrum of the complexes showed signals located at $\delta = 7.90$–8.15 ppm and $\delta = 7.30$–8.08 ppm for Ni(II) and Co(II) complexes, respectively. Aforementioned signals were attributed to the aromatic protons chemical shifts.[34] In the complexes and during the chelation process, the azomethine proton signal of ligands is shifted to low field that affirms the bonding to the metal ions through azomethine nitrogen. Furthermore, the

**Table 3** Magnetic moment for the Schiff base complexes.

| Complexes | $\mu_{eff}$ (B.M) | Geometry |
|---|---|---|
| CoL[1] | 0 | Octahedral |
| CoL[2] | 4.83 | Octahedral |
| CoL[3] | 4.91 | Octahedral |
| NiL[1] | 2.86 | Octahedral |
| NiL[2] | 2.83 | Octahedral |
| NiL[3] | 2.90 | Octahedral |

**Table 4** Mass spectral data of Schiff base ligands and their metal complexes.

| Compound | Cal. mass | Obtained Mass | Peak assigned |
|---|---|---|---|
| $H_2L^1$ | 692.20 | 692 | [M]⁺ |
| $H_2L^2$ | 706.22 | 706 | [M]⁺ |
| $H_2L^3$ | 720.23 | 720 | [M]⁺ |
| CoL[1] | 748.11 | 748 | [M]⁺ |
| CoL[2] | 763.14 | 764 | [M+1]⁺ |
| CoL[3] | 777.15 | 780 | [M+3]⁺ |
| NiL[1] | 748.12 | 750 | [M+2]⁺ |
| NiL[2] | 762.14 | 763 | [M+1]⁺ |
| NiL[3] | 776.15 | 781 | [M+5]⁺ |

**Table 5** Electronic spectral data for the ligands and complexes.

| Compounds | UV-Vis bands /nm | Assignments |
|---|---|---|
| $H_2L^1$ | 279, 369 | $\pi$–$\pi^*$, n–$\pi^*$ |
| $H_2L^2$ | 273, 358 | $\pi$–$\pi^*$, n–$\pi^*$, n–$\pi^*$ |
| $H_2L^3$ | 270, 344 | $\pi$–$\pi^*$, n–$\pi^*$, n–$\pi^*$ |
| CoL[1] | 262, 357<br>407, 586 | $\pi$–$\pi^*$, n–$\pi^*$, n–$\pi^*$<br>d–d |
| CoL[2] | 261, 342<br>405, 577 | $\pi$–$\pi^*$, n–$\pi^*$, n–$\pi^*$<br>d–d |
| CoL[3] | 267, 339<br>416, 581 | $\pi$–$\pi^*$, n–$\pi^*$, n–$\pi^*$<br>d–d |
| NiL[1] | 260, 349<br>416, 868 | $\pi$–$\pi^*$, n–$\pi^*$, n–$\pi^*$<br>d–d |
| NiL[2] | 269, 348<br>423, 875 | $\pi$–$\pi^*$, n–$\pi^*$, n–$\pi^*$<br>d–d |
| NiL[3] | 261, 341<br>417, 860 | $\pi$–$\pi^*$, n–$\pi^*$, n–$\pi^*$<br>d–d |

signal of the phenolic proton in the free ligands was not seen that confirmed the deprotonation of the phenolic group on complexes formation.[20] In ^{1}H-NMR spectra of Co(II) complexes (CoL[2] and CoL[3]), the paramagnetic metal ion effect on chemical shifts is observed. On the contrary, no paramagnetic shifts was seen for CoL[1] that affirms the presence of a Co(III) centre as a result of Co(II) oxidation. The peak observed at $\delta = 3.17$ ppm was because of the bridging –S–CH$_2$–CH$_2$–S– moiety in H$_2$L[1] disappears in the spectrum of CoL[1]. In addition, two new multiplets appeared in the region of $\delta = 5.57$–6.04 ppm were related to the protons of vinyl (–S–CH=CH$_2$).[20] These observations in ^{1}H-NMR spectrum of CoL[1] show the cleavage of C-S bond accompanied by Co[+2] oxidation to Co[+3]. However, no cleavage of C-S bond and metal oxidation occurs in CoL[2] and CoL[3] complexes.

### 3.7. Electrochemical Studies

The pathway of the chemical reactions can be demonstrated by electron transfer as one of the most effective methods. The electrochemical behavior of the ligands, Ni(II) and Co(II) complexes have been investigated by cyclic voltammetry in DMF under argon atmosphere in the potential range from +2.0 to –2.0 V. The CV of ligands show at the range of scan rate of 0.05–0.4 V s^{-1}. It can be observed that there are one cathodic peak and one anodic peak. The E$_p$ and I$_p$ values of the various peaks are listed in Table 6.

The cyclic voltammogram of Ni(II) complexes show at a scan rate of 0.3 V s^{-1}. On comparing the voltammogram of ligands and their Ni(II) complexes, it is evident that the oxidation and reduction peaks appeared in the voltammogram of Schiff bases were totally disappeared on complexation. Thus, the coordination of

Ni(II) causes the ligands to be deactivated. Also, in voltammogram no peak related to Ni(I) and Ni(III) was found.

The cyclic voltammetric curves for the electrochemical reduction of the CoL[1] and CoL[3] exhibit a redox couple, which can be attributed to the reduction of the metal centre. The comparison of the voltammogram of Co(II) complexes shows that the reduction of CoL[1] is harder than CoL[3]. For CoL[1] and CoL[3], the reduction couple (Co[III]/Co[II]) was at –0.475 V and 0.0095 V, respectively, but CoL[2] was inactive (Table 7).

### 3.8. Antibacterial Activity of Ligands and Complexes in Agar Medium

The antibacterial activity of the prepared ligands and complexes was investigated using *Ampicillin* as standard. They affected bacterial species' growth in different manner. The results and the diameter of inhibition zones (mm) are presented in Table 8. Furthermore, the biological activities of the Schiff bases were less than that of the standard, *Ampicillin*. In addition, metal complexes were more effective than the ligands. Nevertheless, this phenomenon is probably because of the more lipophilic feature of the complexes. Additionally, the enhanced metal chelates activity can be clarified based on Overtone's concept and Tweedy's chelation theory.[35] According to Overtone's concept of cell permeability, only the lipid soluble materials are let to pass the lipid membrane surrounding the cell. In this respect, liposolubility is a substantial factor determining the anti-microbial activity. When chelation occurs, an overlap occurs between the orbital of the ligand and metal ion's positive charge partial sharing with donor groups, as a result, the polarity of the metal ion will be reduced as a consequence.[36] Moreover, the $\pi$

**Table 6** Cyclic voltammetric data for Schiff base ligands.

| Ligands | Scan rate /V s$^{-1}$ | E$_a$/v | E$_c$/v | ΔE | E$_{1/2}$ | I$_a$ /μA | I$_c$/μA | I$_a$/I$_c$ |
|---|---|---|---|---|---|---|---|---|
| H$_2$L[1] | 0.05 | 0.1665 | –0.4937 | –0.6602 | –0.1636 | 2.19 | –4.27 | 0.512 |
| H$_2$L[1] | 0.1 | 0.1698 | –0.4966 | 0.6664 | –0.1634 | 3.42 | –6.73 | –0.508 |
| H$_2$L[1] | 0.2 | 0.2034 | –0.5242 | 0.7276 | –0.1604 | 5.67 | –9.97 | –0.568 |
| H$_2$L[1] | 0.3 | –0.2702 | –0.5297 | 0.2595 | –0.3999 | 9.12 | –11.0 | –0.829 |
| H$_2$L[1] | 0.35 | –0.2970 | –0.5020 | 0.2050 | –0.3995 | 11.4 | –11.6 | –0.982 |
| H$_2$L[2] | 0.05 | 0.1372 | –0.4653 | 0.6625 | –0.1640 | 2.35 | –3.70 | –0.6351 |
| H$_2$L[2] | 0.1 | 0.1706 | –0.4985 | 0.6691 | –0.1639 | 4.10 | –7.38 | –0.5555 |
| H$_2$L[2] | 0.2 | 0.1742 | –0.5264 | 0.7006 | –0.1761 | 6.89 | –10.9 | –0.6321 |
| H$_2$L[2] | 0.3 | –0.2995 | –0.5020 | 0.2025 | –0.4007 | 9.82 | –12.5 | –0.7856 |
| H$_2$L[2] | 0.35 | –0.2969 | –0.5624 | 0.2655 | –0.4296 | 9.69 | –11.1 | –0.8729 |
| H$_2$L[3] | 0.05 | 0.2578 | –1.1584 | 1.4162 | –0.4503 | 2.88 | –4.30 | –0.6697 |
| H$_2$L[3] | 0.1 | 0.2611 | –0.6500 | 0.9111 | –0.1944 | 6.41 | –5.07 | –1.264 |
| H$_2$L[3] | 0.2 | 0.2644 | –0.6170 | 0.8814 | –0.1763 | 1.14 | –10.6 | –0.1075 |
| H$_2$L[3] | 0.3 | –0.2993 | –0.5926 | 0.2933 | –0.4459 | 1.41 | –14.8 | –0.0952 |
| H$_2$L[3] | 0.35 | –0.2049 | –0.6253 | 0.4204 | –0.4151 | 23.9 | –16.7 | –1.43 |

E$_a$ = anodic potential; E$_c$ = cathodic potential; ΔE = E$_a$-E$_c$ E$_{1/2}$ = 1/2[E$_a$+E$_c$] I$_a$ = anodic current; I$_c$ = cathodic current.

**Table 7** Cyclic voltammetric data for Co(II) complexes.

| Complexes | Scan rate /V s$^{-1}$ | E$_c$/v | E$_a$/v | ΔE | E$_{1/2}$ | I$_a$ /μA | I$_c$ /μA | I$_a$/I$_c$ |
|---|---|---|---|---|---|---|---|---|
| CoL[1] | 0.05 | –0.545 | –0.404 | 0.141 | –0.4745 | 2.30 | –4.07 | –0.565 |
| CoL[1] | 0.1 | –0.548 | –0.371 | 0.177 | –0.4595 | 3.30 | –5.69 | –0.579 |
| CoL[1] | 0.2 | –0.563 | –0.356 | 0.207 | –0.4595 | 4.16 | –8.15 | –0.510 |
| CoL[1] | 0.3 | –0.569 | –0.349 | 0.220 | –0.4590 | 5.07 | –10.3 | –0.492 |
| CoL[3] | 0.05 | –0.0365 | 0.0555 | 0.092 | 0.0095 | 1.55 | –1.09 | –1.422 |
| CoL[3] | 0.1 | –0.0398 | 0.0589 | 0.0987 | 0.00955 | 2.30 | –1.71 | –1.345 |
| CoL[3] | 0.2 | –0.0716 | 0.06423 | 0.1358 | –0.00368 | 3.40 | –2.58 | –1.317 |
| CoL[3] | 0.3 | –0.0779 | 0.0710 | 0.1489 | –0.00345 | 4.17 | –3.20 | –1.3031 |

**Table 8** Antibacterial activity of ligands and complexes.

| Compound /5 mg L$^{-1}$ | *Escherichia coli* /mm | *Staphylococcus aureus* /mm | *Bacillus subtilis* /mm |
|---|---|---|---|
| H$_2$L$^1$ | 10.6 | 13.4 | – |
| H$_2$L$^2$ | 12.1 | 12.9 | – |
| H$_2$L$^3$ | 9.8 | 11.6 | – |
| CoL$^1$ | 19.4 | 17.2 | – |
| CoL$^2$ | 17.2 | 17.6 | – |
| CoL$^3$ | 16.1 | 18.3 | – |
| NiL$^1$ | 13.1 | 19.6 | – |
| NiL$^2$ | 14.7 | 20.3 | – |
| NiL$^3$ | 14.9 | 20.5 | – |
| Ampicillin | 21.2 | 22.4 | 30.6 |

electrons over the chelate ring will be further delocalized leading to higher lipophilicity of the complex. As a consequence, the complexes will penetrate into lipid membrane more, so the microorganism's enzymes binding sites will be blocked. In addition, respiration process of the cells can be disrupted by metal complexes, as a consequent, the synthesis of proteins will be blocked and growth of the organism will be limited.[37] The effectiveness of complexes against organisms relies on the impermeability of the microbe's cells or difference in ribosomes of microbial cells. Furthermore, the data showed that *Escherichia coli* and *Staphylococcus aureus* were been inhibited in a greater degree by the Co(II) and Ni(II) complexes respectively; however, none of the compounds were active against *Bacillus subtilis*.

## 4. Conclusions

In this research, Schiff base ligands and prepared complexes with Ni(II), Co(II) ions were successfully synthesized and characterized. The analytical results showed 1:1 metal:ligand stoichiometry. According to the elemental CHNS analysis, FT-IR, $^1$H-NMR spectral studies, Schiff base ligands acted as N$_2$O$_2$S$_2$ ligands. The molar conductance values in complexes revealed the presence of non-electrolytic compounds (except CoL$^1$ that is electrolyte). The magnetic moments and electronic spectra studies suggested an octahedral structure. Reaction of H$_2$L$^1$ with Co(II) salt resulted in oxidative cleavage of the C–S bond to produce a Co(III) product. In addition, the effects of prepared ligands and complexes were investigated on some bacteria such as *Escherichia coli*, *Staphylococcus aureus* and *Bacillus subtilis*. Synthesized complexes exhibited appropriate antibacterial effect.

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## References

1 R.K. Al-Shemary, A.M.A. Al-Khazraji and A.N. Niseaf, Preparation, spectroscopic study of Schiff base ligand complexes with some metal ions and evaluation of antibacterial activity, *Pharm. Innov. J.*, 2016, **5**, 81–86.
2 G. Kumar, D. Kumar, C.P. Singh, A. Kumar and V.B. Rana, Synthesis, physical characterization and antimicrobial activity of trivalent metal Schiff base complexes, *J. Serb. Chem. Soc.*, 2010, **75**, 629–637.
3 L. Kafi-Ahmadi, A. Poursattar Marjani and M. Pakdaman-Azari, Synthesis, characterization and antibacterial properties of *N,N*-bis(4-dimethylaminobenzylidene)benzene-1,3-diamine as new Schiff base ligand and its binuclear Zn(II), Cd(II) complexes, *S. Afr. J. Chem.*, 2018, **71**, 155–159.
4 A.P. Sangamesh, T.P. Chetan, M.H. Bhimashankar, S.T. Shivakumar and S.B. Prema, DNA cleavage, antibacterial, antifungal and anthelmintic studies of Co(II), Ni(II) and Cu(II) complexes of coumarin Schiff bases: synthesis and spectral approach. *Spectrochim Acta A.*, 2015, **137**, 641–651.
5 M.A. Mokhles, A.L. Ammar, A.M. Hanan, A.M. Samia, M.A. Mamdouh and A.E. Ahmed, Synthesis, anticancer activity and molecular docking study of Schiff base complexes containing thiazole moiety, *Beni-Seuf Univ. J. Appl. Sci.*, 2016, **5**, 85–96.
6 *M. Kumar*, T. Padmini and K. Ponnuvel, Synthesis, characterization and antioxidant activities of Schiff bases are of cholesterol, *J. Saudi. Chem. Soc*, 2017, **21**, S322–S328.
7 L. Jia, J. Xu, X. Zhao, Sh. Shen, T. Zhou, Z. Xu, T. Zhu, R. Chen, T. Ma, J. Xie, K. Dong and J. Huang, Synthesis, characterization, and antitumor activity of three ternary dinuclear copper(II) complexes with a reduced Schiff base ligand and diimine coligands in vitro and in vivo, *J. Inorg. Biochem.*, 2016, **159**, 107–119.
8 J.F. Adediji, E.T. Olayinka, M.A. Adebayo and O. Babatunde, Antimalarial mixed ligand metal complexes: synthesis, physicochemical and biological activities, *Int. J. Phys. Sci.*, 2009, **4**, 529–534.
9 E.L. Chang, C. Simmers and D.A. Knight, Cobalt complexes as antiviral and antibacterial agents, *Pharmaceuticals*, 2010, **3**, 1711–1728.
10 N. Chantarasiri, T. Tuntulani, P. Tongraung, R. Seangprasertkit-Magee and W. Wannarong, New metal-containing epoxy polymers from diglycidyl ether of bisphenol A and tetradentate Schiff base metal complexes, *Eur. Poly. J.*, 2000, **36**, 695–702.
11 I.P. Oliveri, S. Failla, G. Malandrino and S. Di Bella, New molecular architectures by aggregation of tailored zinc(II) Schiff-base complexes, *New J. Chem.*, 2011, **35**, 2826–2831.
12 S.Gh. Musharraf, A. Bibi, N. Shahid, M. Najam-ul-Haq, M. Khan, M. Taha, U.R. Mughal and Kh.M. Khan, Acylhydrazide and isatin Schiff bases as alternate UV-laser desorption ionization (LDI) matrices for low molecular weight (LMW) peptides analysis, *Am. J. Analyt. Chem.*, 2012, **3**, 779–789.
13 P. Kathirgamanathan, S. Surendrakumar, J. Antipan-Lara, S. Ravichandran, Y.F. Chan, V. Arkley, S. Ganeshamurugan, M. Kumaraverl, G. Paramswara, A. Partheepan, V.R. Reddy, D. Bailey and A.J. Blake, Novel lithium Schiff-base cluster complexes as electron injectors: synthesis, crystal structure, thin film characterisation and their performance in OLEDs, *J. Mater. Chem.*, 2012, **22**, 6104–6116.
14 A. Wachi, Y. Kudo, A. Kanesaka, H. Nishikawa, T. Shiga, H. Oshio, M. Chikamatsu and R. Azumi, Organic field-effect transistor based on paramagnetic Cu(II) neutral complexes coordinated by Schiff base-type TTF ligands, *Polyhedron.*, 2017, **136**, 70–73.
15 V. Nishal, D. Singh, R.K. Saini, V. Tanwar, S. Kadyan, R. Srivastava and P.S. Kadyan, Characterization and luminescent properties of zinc-Schiff base complexes for organic white light emitting devices, *Cogent Chem.*, 2015, **1**, 1079291.
16 S.G. Rosenfield, W.H. Armstrong and P.K. Mascharak, Convenient synthesis and properties of (R$_4$N)$_2$[Ni(SAr)$_4$](Ar = C$_6$H$_5$, *p*-C$_6$H$_4$Cl, *p*-C$_6$H$_4$CH$_3$, and *m*-C$_6$H$_4$Cl) and the structure of tetra ethyl ammonium tetra kis(*p*-chlorobenzenethiolato)nickelate(II), *Inorg. Chem.*, 1986, **25**, 3014–3018.
17 W. Rosen and D.H. Busch, Octahedral nickel(II) complexes of some cyclic polyfunctional thioethers, *Inorg. Chem.*, 1970, **9**, 262–265.
18 S. Chandrasekhar and A. McAuley, Syntheses and reactivity of nickel complexes of 8-aza-1,5-dithiacyclodecane and the macrobicyclic ligand 1,2-bis(8-aza-1,5-dithia-8-cyclodecanyl)ethane, *Inorg. Chem.*, 1992, **31**, 2234–2240.

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L. Kafi-Ahmadi and A. Poursattar Marjani,
*S. Afr. J. Chem.*, 2019, **72**, 101–107,
<http://journals.sabinet.co.za/content/journal/chem/>.

107

19  C.P. Kulatilleke, S.N. Goldie, M.J. Hegg, L.A. Ochrymowycz and D.B. Rorabacher, Formation and dissociation kinetics and crystal structures of nickel(II)–macrocyclic tetrathiaether complexes in acetonitrile. Comparison to nickel(II)–macrocyclic tetramines, *Inorg. Chem.*, 2000, **39**, 1444–1453.

20  G. Rajsekhar, C.P. Rao, P. Saarenketo, K. Nattinen and K. Rissanen, Complexation behaviour of hexadentate ligands possessing $N_2O_4$ and $N_2O_2S_2$ cores: differential reactivity towards Co(II), Ni(II) and Zn(II) salts and structures of the products, *New. J. Chem.*, 2004, **28**, 75–84.

21  A. Reiss, A. Samide, G. Ciobanu and I. Dabuleanu, Synthesis, spectral characterization and thermal behaviour of new metal(II) complexes with Schiff base derived from amoxicillin, *J. Chil. Chem. Soc.*, 2015, **60**, 3074–3079.

22  M.K.B. Break, M.I.M. Tahir, K.A. Crouse and T.J. Khoo, Synthesis, characterization, and bioactivity of Schiff bases and their $Cd^{2+}$, $Zn^{2+}$, $Cu^{2+}$ and $Ni^{2+}$ complexes derived from chloroacetophenone isomers with S-benzyldithiocarbazate and the X-Ray crystal structure of S-benzyl-$\beta$-N-(4-chlorophenyl)methylenedithiocarbazat, *Bioinorg. Chem. Appl.*, 2013, **2013**, 1–13. DOI: 10.1155/2013/362513

23  R. Arab Ahmadi and S. Amani, Synthesis, spectroscopy, thermal analysis, magnetic properties and biological activity studies of Cu(II) and Co(II) complexes with Schiff base dye ligands, *Molecules*, 2012, **17**, 6434–6448.

24  N.P. Singh, P. Saini and A. Kumar, Synthesis and spectroscopic characterization of some novel Schiff base compounds of transition metal and their biological studies, *RJC*, 2013, **6**, 190–195.

25  H.A. Bayoumi, Characteristic studies of hexamethylene diamine complexes, *Inter. J. Inorg. Chem.*, 2013, **2013**, 1–12. DOI: 10.1155/2013/458018

26  R.J. Angelici, *Synthesis and Technique in Inorganic Chemistry*, 2nd edn., Saunders Company, 1977, p 221.

27  M.A. Ali, A.H. Mirza and R.J. Butcher, Synthesis and characterization of Copper(II) complexes of the methyl pyruvate Schiff base of S-methyldithiocarbazate (HMPSME) and the X-crystal structures of HMPSME and [Cu(MPSME)Cl], *Polyhedron*, 2001, **20**, 1037–1043.

28  S. Jyothi, K. Sreedhar, D. Nagaraju and S.J. Swamy, Synthesis and spectral investigation of Co(II), Ni(II), Cu(II) and Zn(II) complexes with novel N4 ligands, *Can. Chem. Tran.*, 2015, **3**, 368–380.

29  N.K. Chaudhary and P. Mishra, Metal complexes of a novel Schiff base based on penicillin: characterization, molecular modeling, and antibacterial activity study, *Bioinorg. Chem. & Appl.*, 2017, **2017**, 1–13. DOI: 10.1155/2017/6927675

30  C.R. Hammond, The Elements, In *Handbook of Chemistry and Physics*, 1st edn., New York. 2000.

31  A.S. Abu-Khadra, R.S. Farag and A.El.M. Abdel-Hady, Synthesis, characterization and antimicrobial activity of Schiff base (E)-*N*-(4-(2-hydroxybenzylideneamino)phenylsulfonyl) acetamide metal complexes, *AJAC*, 2016, **7**, 233–245.

32  N.H. Al-Saadawy, F.F. Alyassin and H.R. Faraj, Preparation and characterization of some new complexes of Schiff bases derived from benzoin and glycine, *GJPACR*, 2016, **4**, 13–20.

33  M. Shibata and H. Kandori, FTIR studies of internal water molecules in the Schiff base region of bacteriorhodopsin, *Biochemistry*, 2005, **44**, 7406–7413.

34  J.G. Gilbert, A.W.W. Addison and R.J. Butcher, Some nickel(II) complexes with pentadentate and tridentate heterocyclic N- and S-donor ligands, *Inorg. Chim. Acta.*, 2000, **308**, 22–30.

35  B.G. Tweedy, Plant extracts with metal ions as potential antimicrobial agents, *Phytopathology*, 1964, **55**, 910–914.

36  J. Parekh, P. Inamdhar, R. Nair, S. Baluja and S. Chanda, Synthesis and antibacterial activity of some Schiff bases derived from 4-aminobenzoic acid, *J. Serb. Chem. Soc.*, 2005, **70**, 1155–1161.

37  Y. Vaghasia, R. Nair, M. Soni, S. Baluja and S. Chanda, Synthesis, structural determination and antibacterial activity of compounds derived from vanillin and 4-aminoantipyrine, *J. Serb. Chem. Soc.*, 2004, **69**, 991–998.